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Research has been carried out in two areas: heterogeneous catalysis and materials for energy storage. In the first project, standard batches of Pt/SiO_2 catalysts were prepared and characterized utilizing a variety of techniques, e.g., x-ray diffraction, isotopic exchange between deuterium and cyclopentane, etc. The purpose of these studies is to elucidate information on the nature of the catalyst crystallites, the effect of the support upon the catalyst behavior, the effect of metallic particle size on catalytic

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characteristics and the effect of the method of catalyst preparation upon catalytic activity. The results of the final sets of measurements are presented.

In the second project, a number of materials have been synthesized for possible use as solid state electrolytes and electrodes. Mössbauer and NMR techniques have been used to screen and characterize these materials. Further efforts were made to characterize the most promising of the fast Li^+ ion conductors, $Li_2Ti_3O_7$. In addition, studies on the cuprous halides as model systems were completed, and the role of a dispersed second phase on the ionic and electronic conductivity investigated further. Lastly, the sintering studies to develop a porous ceramic for use as a separator to retain the molten electrolyte in the cell were continued.

A number of the publications resulting from this research are listed at the end of this report.

FINAL TECHNICAL REPORT

July 1, 1976 - June 30, 1977

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Title: Basic and Applied Research in Materials

Materials Research Center
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Evanston, Illinois 60201

I. SUMMARY

This report covers the period 1 July 1976 through 30 June 1977 and represents the Final Technical Report for this contract. Research has been carried out in two major areas: 1) Materials for Energy Storage and 2) Heterogeneous Catalysis. During this final year of the project, funding was at the level of $60,000, and the technical results reflect this decreased effort. The research reported herein is intended to complement that of the previous Annual Report.

A. Research Program Plan

1. Materials for Energy Storage

The discovery of new types of solid electrolytes (such as beta alumina, $RbAg_4I_5$, copper and silver halides and stabilized zirconia) with large values of ionic conductivity at relatively low temperatures has enhanced the prospect of developing battery systems possessing a high energy storage-to-weight ratio, high power output capability, long life in service, efficiency in charge-discharge characteristics and the capability of being constructed from inexpensive, readily obtainable materials. Three complementary areas of research are being pursued. The first involves a search for new materials to be used as solid state electrolytes and electrodes; the second involves detailed studies on electrolytes already known to be predominantly ionic conductors, and the third involves a fundamental investigation of sintering and hot pressing of materials of interest. Toward these ends, the studies on the cuprous halides as model systems are being completed, and the role of a dispersed second phase on the ionic and electronic conductivity investigated further. The search for electrolyte materials is being concentrated on the mixed halides. Mössbauer and NMR techniques are being used to characterize these materials. In addition, the fast Li^+ ion conductor $Li_2Ti_3O_7$ was characterized more completely. The sintering studies are being pursued in order to develop methods of preparing dense, polycrystalline electrolytes and electrode materials as well as to prepare porous ceramic materials capable of serving as a separator in a cell utilizing a molten lithium salt.

2. Heterogeneous Catalysis

A number of the most important heterogeneous catalysts consist of tiny crystallites of metal supported upon a carrier such as silica or alumina. The support leads to a greater metallic surface area per gram of metal and permits use of the catalyst at temperatures up to 500°C without rapid sintering. However, relatively little is known of the exact nature of the crystallites (including the nature of their attachment to the support), the effect of the support upon the catalyst behavior, the effect of metallic particle size on catalytic characteristics and the effect of the method of catalyst preparation upon catalytic activity. It is the purpose of this project to provide some resolution of these problems.

Standard batches of catalysts are being prepared by different methods, of varying particle sizes and on different supports. These catalysts will be characterized as completely as possible using x-ray diffraction and scanning and transmission electron microscopy studies (to determine crystallite size, orientation, strain, dislocation density and radial density function), EPR studies (to yield information about the migration of reactants and products on the support and, possibly, the nature of the catalytic sites on the metal), kinetic studies (to determine the kinetic form and rate constants for reactions chosen to give optimum information about catalytic characteristics) and selectivity studies (to determine relative yields of several concurrent reactions). Analytical studies will be undertaken to correlate the data on the two sets of catalysts to be studied (on silica and alumina supports) in this project and to develop a theoretical understanding of the underlying phenomena.

B. Technical Results

1. Materials for Energy Storage

Work has continued on the development of a porous ceramic for use as a separator to retain the molten electrolyte in the desired configuration within the cell. Accordingly, microstructure development and mechanical property--microstructure dependencies of sintered Y_2O_3 were investigated. Fine grain samples of Y_2O_3 have been prepared utilizing an organic precursor technique. Specimens of 46% porosity were obtained with a homogeneous open channel porosity of ~ 0.5 μm diameter and a Vickers apparent microhardness of 650 MPa under a 215 gram load.

A variety of lithium containing salts have been screened for use as electrolytes in the above cell. The most promising candidates, the mixed halides in the systems $LiCl-CdCl_2$, $LiBr-CdBr_2$ and $LiCl-MgCl_2$, were prepared and a number of experiments performed to determine their suitability as electrolyte materials.

Further efforts have been made to characterize the compound $Li_2Ti_3O_7$, the most promising of the fast Li^+ ion conductors synthesized. Dielectric loss measurements on polycrystalline samples revealed that the loss process had an activation energy of about 0.4 eV and an attempt frequency of about $10^{12}s^{-1}$. Two probe ac conductivity measurements using blocking silver and carbon electrodes on the best samples showed that an activation energy of about 0.48 eV was characteristic for the temperature range $\approx 20^o - 200^oC$. Room temperature conductivity of the polycrystalline materials, measured at 20 KHz, was about $10^{-6}ohm^{-1}cm^{-1}$.

AC conductivities were measured for a class of compounds based on the copper halides. The most notable of these compounds is $RbCu_4Cl_5$, which exhibited an ac conductivity of $8.25 \times 10^{-5}ohm^{-1}cm^{-1}$ at 25°C and 1.14×10^{-2} $ohm^{-1}cm^{-1}$ at 140°C. These values are higher than any previously reported for copper-inorganic electrolytes and are comparable to those previously reported for copper-organic compounds. The compound $RbCu_3Cl_4$ exhibited a copper ion conductivity $\sigma = 2.25 \times 10^{-3}ohm^{-1}cm^{-1}$ at 25°C and a low electronic conductivity of $< 10^{-5}ohm^{-1}cm^{-1}$.

Studies on the role of a dispersed second phase of "inert particles" on the ionic and electronic conductivity of a solid state electrolyte, CuCl, were continued. A model was developed using the concept of a space charge layer around each dispersed particle which accounts for the observed increased conductivity.

2. Heterogeneous Catalysis

In the isotopic exchange between deuterium and cyclopentane at 50 - 81°C, the activity decays rather rapidly with the time of the run. Experiments on the nature of the hydrocarbon layer that forms on the catalyst showed that some form of strongly absorbed cyclopentane is the principal inhibitor of the isotopic exchange.

Heating the catalysts in oxygen at 300°C increases the surface content in oxygen. Unlike a clean catalyst treated with oxygen at 25°C, the surface oxide created at 300°C is incompletely removed by 5 pulses of hydrogen at 25°C. Further studies demonstrated that the effect is structure sensitive.

The effects of pretreatment procedures on the activity for methylcyclopropane hydrogenation for a series of the Pt/SiO_2 catalysts were determined. Hydrogenation activity was enhanced by low temperature reduction for the catalysts of lower dispersion, while high temperature reduction enhanced activity of the high dispersion samples. While the activity levels are affected by pretreatment procedures, preliminary results indicate that the activation energy is unaffected.

In order to cancel the small angle x-ray scattering from the Pt-silica gel and measure the surface area of the Pt alone, two promising organic liquids are being tested, which have the same electron density as the gel. Additional x-ray measurements of the mean square thermal vibrations of the Pt atoms in the catalysts have been made using the 220 peak at both room temperature and 77°K for a sample of 27% dispersion. These results substantiate those obtained previously, which showed a large increase in thermal vibrations with decreasing size.

II. RESEARCH REPORTS

A. Materials for Energy Storage

Faculty:

D. H. Whitmore, Professor, Materials Science and Engineering
Group Leader
D. L. Johnson, Professor, Materials Science and Engineering
J. B. Wagner, Jr., Professor, Materials Science and Engineering

Research Staff:

T. Matsui, Postdoctoral Research Associate
W. A. Spurgeon, Postdoctoral Fellow

Graduate Students:

D. Hankey, Materials Science and Engineering
T. Jow, Materials Science and Engineering
D. King, Materials Science and Engineering

The purpose of this research is to identify promising fast ion conductors for use as electrolytes and to develop separators utilizing these electrolytes for relatively low temperature battery applications.

Several of the advanced battery systems presently being considered for load leveling or vehicular propulsion are operative at temperatures considerably above ambient. Two of the most widely investigated systems are the sodium-sulfur and lithium-sulfur batteries.

The sodium-sulfur battery operates at temperatures of 350°C so as to keep the polysulfide cathode material molten, thus reducing polarization effects. The high temperature of operation also gives the sodium beta- or beta″-alumina solid electrolyte a favorable conductivity.

The battery utilizing the lithium-sulfur system is operative at 425°C, this temperature being dictated by the melting point of the molten salt electrolyte used. With early cells this temperature of operation not only presented corrosion problems but also caused instabilities in the electroactive materials at this temperature of operation. In particular, sulfur volatilization at the cathode and corrosion by lithium of the anode components dictated that the chemical activities of these materials be reduced, leading to the system $LiAl/FeS_2$. This has had, however, the effect of reducing the cell voltage from 2.3 to 1.6 and the theoretical energy density from 1200 to 364 Wh/lb. It would be highly desirable, therefore, to lower the temperature of operation of the lithium-sulfur system so that the use of lithium and sulfur each of unit activity could be used.

One approach to the solution of this problem would be the identification and fabrication of a lithium ion conductive ceramic of high conductivity at a temperature lower than that of the present lithium-sulfur battery.

Professor D. L. Johnson has suggested an innovative and technically feasible approach to solving the problem of a fast Li^+ ion conductor which operates at a temperature not too far removed from the ambient. Basically, Professor Johnson's idea is to sinter a thin, inert ceramic body (the separator) to a given degree of open porosity and then to infiltrate this body with a molten lithium-bearing salt which will wet the ceramic separator. In this scheme, the lithium salt must be a fast Li^+ ion conductor since it functions as the electrolyte and the separator provides mechanical support and retains the electrolyte phase in the desired configuration in the cell.

The ceramic chosen for the porous separator was Y_2O_3, dictated primarily by the requirement that it be stable with respect to molten Li, as observed by Singh [R. N. Singh, J. Amer. Ceram. Soc. 59, 112 (1976)] and be an electronic insulator. Professor Johnson's student investigated microstructure development and preliminary mechanical property-microstructure dependencies of sintered porous Y_2O_3.

An organic precursor technique [C. Marcilly, P. Courty and B. Delmond, J. Amer. Ceram. Soc. 53, 56 (1970)] was employed to prepare ultra fine grain (200 - 260 Å) Y_2O_3. Relatively low sintering temperatures of 1200 - 1400°C with times up to 168 hours were used in an attempt to maximize strengthening of the porous compacts with minimum densification. It was found that compacts of 260 Å starting particle size powder sintered at 1400°C for four hours possessed the best properties obtained, namely 46% porosity, a Vickers apparent microhardness of 650 MPa under a 215 g load, and a homogeneous open channel porosity of $\sim 0.5\ \mu m$ diameter.

Professor Whitmore's group has investigated various lithium-containing salts which might have potential as the electrolyte phase in the cell described above. Preliminary screening of such electrolyte candidates, using ac conductivity measurements, were undertaken on the following materials: Li_2SnCl_4, Li_2CdI_4, $LiI \cdot Li_2SO_4$, $LiBr \cdot SrBr_2$, $LiI \cdot LiOH$, $LiF \cdot LiOH$, $LiBr \cdot LiOH$, Li_2CaI_4, $4LiI \cdot Li_2WO_4$, $5Li_2SO_4 \cdot Rb_2SO_4$, $Li_2SO_4 \cdot Rb_2SO_4$, $Li_2SO_4 \cdot Rb_2SO_4$, $Li_2SO_4 \cdot CaSO_4$, $Li_2SO_4 \cdot Na_2SO_4$, $LiAlCl_4$, Li_2ZnCl_4, Li_2MnCl_4 and $7LiCl \cdot 4BaCl_2 \cdot 10RbCl$.

The most promising candidates were mixed halides in the systems $LiCl$-$CdCl_2$, $LiBr$-$CdBr_2$ and $LiCl$-$MgCl_2$ systems. After preparation of the mixed halides by fusing the simple salts in the correct proportions under a halide gas atmosphere, the following experiments were performed: (1) DTA runs between 298° and 673°K to establish if phase transformations occurred in this temperature range; (2) NMR motional narrowing experiments of the ^7Li

resonance line between 77° and 700°K to establish whether or not fast Li^+ ion mobility occurred; (3) total ac conductivity measurements from 298°K to the melting temperature to establish whether the Li^+ ion motion was, indeed, long-range and the magnitude of the electrical conductivity as a function of temperature; (4) x-ray diffraction powder pattern experiments to determine whether the material was homogeneous or multi-phased; and (5) experiments to obtain a measure of the Li^+ ion transference number as a function of temperature using cells of the type Li | Mixed Halide Phase | AgI, Ag.

Neither the electrical conductivity nor the DTA results revealed any phase transformations between room temperature and the melting temperature for the compositions $LiCl$-$CdCl_2$(50 w/o LiCl), $LiCl$-$CdCl_2$(31.8 w/o LiCl), $LiCl$-$MgCl_2$(44 w/o LiCl) and the double salt Li_2CdI_4. In contrast, the compounds $Li_{1.6}Cd_{0.2}Br_2$, $Li_{1.0}Cd_{0.5}Br_2$ and $Li_{0.6}Cd_{0.7}Br_2$ did exhibit apparent phase transformations at about 227°, 185° and 259°C, respectively; the conductivity in the high-temperature modification of each compound ranged from 10^{-2} $(\Omega\text{-cm})^{-1}$ upwards. The conductivity of the double salt, Li_2CdI_4 is also high $[\approx 10^{-1}(\Omega\text{-cm})^{-1}]$ around 225°C, but like most of these materials exhibited some instability when placed in contact with lithium.

Another phase of our program dealing with fast Li^+ ion conductors involved a search by Professor Whitmore's group for oxide phases which exhibited the possibility of Li^+ ion motion in either tunnels or channels present in the crystalline structure. Numerous lithium germanates, titanates, manganates, zirconates, stannates and aluminates were synthesized by standard ceramic techniques and screened by NMR motional-narrowing and electrical conductivity techniques. In most cases, the conductivities exhibited by these compounds in range 300 - 400°C were too low for them to be given serious consideration as the electrolyte in a Li/S secondary battery system and hence no further work was undertaken on them.

However, because NMR line-narrowing measurements indicated that rapid Li^+ motion occurs in the compound $Li_2Ti_3O_7$, further efforts were made to characterize this material and assess its potential as an electrolyte. This compound has an orthorhombic crystal structure known as ramsdellite in which edge-sharing TiO_6 octahedra form linear tunnels which contain the Li^+ ions. Various ceramic processing techniques were tried in attempts to obtain high-density, polycrystalline $Li_2Ti_3O_7$ samples, the most satisfactory results being obtained with an organic precursor technique. X-ray powder patterns obtained with CuKα radiation on samples, so prepared, revealed unit cell dimensions in agreement with those reported in the literature. Chemical analysis for lithium by atomic adsorption, indicates that the lithium concentration of the compound is within 3% of the expected value.

Preliminary dielectric loss measurements done on the $Li_2Ti_3O_7$ polycrystalline samples revealed that the loss process had an activation energy of about 0.4 eV and an attempt frequency of about $10^{12}s^{-1}$; although this phenomenon is likely to be the result of Maxwell-Wagner losses in the $Li_2Ti_3O_7$, further study is needed to confirm this.

Two-probe ac conductivity measurements were performed on the best samples prepared by Professor Whitmore's group using blocking silver and carbon electrodes; these showed that an activation energy of about 0.48 eV was characteristic of the data observed in the temperature range from 20° to 200°C. The room-temperature conductivity of the polycrystalline material, measured at 20 KHz, was about $10^{-6}ohm^{-1}cm^{-1}$. A similar room-temperature conductivity value was found when a solution of lithium iodide in propylene carbonate was applied to opposite faces of the sample as reversible electrodes.

Professor Wagner's group has studied a class of compounds that exhibit high ionic conductivity. These were based on the copper halides. The ac electrical conductivity has been measured for the systems: $CuI + CdI_2$; $CuCl + CdCl_2$; CuI + KI; CuI + RbI and CuCl + RbCl. All of these systems exhibited appreciable copper ion conductivity. The compounds, KCu_4I_5, $Rb_2Cu_3Cl_5$ and $RbCu_4Cl_5$ (80 mole % CuCl) were surveyed, and these exhibited high conductivity, especially $RbCu_4Cl_5$ which exhibited exceptionally high conductivity even at room temperature. For example, the ac conductivity amounted to $8.25 \times 10^{-5}\ \Omega^{-1}cm^{-1}$ at 25°C and $1.14 \times 10^{-2}\ \Omega^{-1}cm^{-1}$ at 140°C. These conductivity values are higher than any other values reported for copper-inorganic electrolytes, and they are comparable to those previously reported for the copper-organic compounds. Furthermore, the $RbCu_4Cl_5$ appears to be more stable than the copper-organic compounds. The compound, $RbCu_3Cl_4$ (75 mole percent CuCl) exhibited even higher copper ion conductivity ($\sigma = 2.25 \times 10^{-3}\ \Omega^{-1}cm^{-1}$) at 25°C and a very low ($< 10^{-5}\ \Omega^{-1}cm^{-1}$) electronic conductivity.

This class of compounds represents a new class of fast copper ion conductors--the so-called superionic conductors--and they are analogous to the MRb_4I_5 (M = K, Rb or NH_3) fast silver ion conductors.

In a parallel study, Professor Wagner's group studied the role of a dispersed second phase of "inert particles" on the ionic and electronic conductivity of a solid state electrolyte, CuCl. Submicron dispersoids of Al_2O_3 were embedded in CuCl, and the resulting electrical conductivities were measured as a function of particle size, volume fraction of dispersoid and temperature. They found that the addition of a dispersoid which did <u>not</u> dissolve in the matrix increased the low temperature ionic conductivity by one order of magnitude or higher while not significantly changing the very low electronic conductivity. A model was developed using the concept of a space charge layer around each dispersed particle which accounted for the increased conductivity. The result was that the change in conductivity, $\Delta\sigma$, caused by the dispersoid of radius r_1 was given by

$$\Delta\sigma \cong 3 \sum_i e\, u_i \langle \Delta n_i \rangle \lambda \cdot \frac{1}{r_1} \left[\frac{V_v}{1 - V_v}\right]$$

where r_1 is much less than r_2, the radius of volume encompassing the particle, e is the electronic charge, u_i the mobility of the ith species, Δn_i the change in the number of mobile species, λ a parameter describing the thickness (radial) of the space charge layer, and V_v the volume fraction of the added dispersoid. This model satisfactorily accounted for the observed data. The significance of their study is that the low temperature ionic conductivity of a solid electrolyte may be enhanced by the introduction of a dispersed, sub-micron size, second phase.

The electrical properties of a lithium containing compound, $LiFe_5O_8$, were also studied. This compound conducted both ionically and electronically. While it is unsuitable as a solid electrolyte, it may have potential use as an electrode.

B. Heterogeneous Catalysis

Faculty:

R. L. Burwell, Jr., Professor, Chemistry, Group Leader
J. B. Butt, Professor, Chemical Engineering
J. B. Cohen, Frank C. Engelhart Professor of Materials Science and Engineering

Research Staff:

Y. Inoue, Postdoctoral Fellow
S. Sashital, Visiting Scholar
J. Solomon, X-Ray Specialist
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Graduate Student:

P. Schipper, NSF Energy Trainee, Chemical Engineering

Metallic catalysts of Group VIII such as platinum, palladium and nickel are of major importance both scientifically and technologically. A number of the most important catalysts consist of tiny particles of metal supported upon a carrier such as silica or alumina. The use of a support leads to a greater metallic surface area per gram of metal since on the support crystallite sizes can be as small as 15 to 150 Å. Furthermore, the presence of the support permits the catalyst to be used at temperatures up to 500° without rapid sintering and consequent loss of metallic area.

Supported catalysts are essential to the production of products in the petroleum and chemical industries. Moreover, improvements in heterogeneous catalysis offer prospects of substantial reductions in the consumption of fuel. Although much is known about supported catalysts, relatively little is known concerning: 1) the exact nature of the crystallites, i.e., size, shape and nature of the attachment to the support; 2) the effect of the support upon the detailed catalytic characteristics of the metal; 3) the effect of metallic particle size and shape upon the catalytic characteristics; and 4) the effect of the method of catalyst preparation upon the details of catalytic activity.

Platinum catalysts were chosen for the initial studies, because there is more background information available for them than for other metals, they are less easily poisoned, and the procedure for the measurement of dispersion (percentage of surface atoms of the metal crystallites) appears to be better defined. Silica was chosen as the first support material to be studied, primarily because it is the most inert of the materials commonly used as catalyst supports.

In previous reports, the preparation of a set of platinum on silica gel catalysts was described, and measurements of the dispersion (the fraction of total platinum atoms which are on the surface) of these catalysts were presented. Results of an investigation of the rates of formation and of the isotopic distribution patterns of the cyclopentanes which result from isotopic exchange between cyclopentane and deuterium were also given, as were those of studies on deactivation and selectivity. The activity and selectivity of these catalysts were also determined for hydrogenation of propylene and methycyclopentane, and the catalysts were characterized by means of x-ray diffraction studies. The results of the final measurements performed in this sequence are presented below.

In the first study on the heterogeneous catalysis, two areas were investigated by Professor Burwell's group during this period. In isotopic exchange between deuterium and cyclopentane at 50 - 81°C, the activity decays rather rapidly with the time of the run. To study the nature of the hydrocarbon layer which forms on the catalyst and inhibits the reaction, at the end of a run at 81°C the catalyst was flushed with helium for 20 min. The catalyst temperature was then raised progressively to 450°C and the effluent gas was analyzed. No hydrocarbons were found at temperatures to 100°C. Between 100 and 450°C, 0.48 CH_4 per surface atom of Pt was evolved. In other experiments, hydrogen was substituted for helium at the end of the 20 min flush with helium. Large amounts of cyclopentane were evolved between 81 and 100°C, nothing between 100 and 200°C, and 0.05 CH_4 between 200 and 450°C. These findings show that some form of strongly adsorbed cyclopentane is the principal inhibitor of the isotopic exchange. The treatment in hydrogen to 450°C restores the catalytic activity.

In the second, heating the catalysts in oxygen at 300°C increases the surface content in oxygen. The quantity of surface oxide was measured by trapping a pulse of hydrogen at 25 or 100°C in the catalytic reactor and then releasing it for measurement after an appropriate period of time. Unlike a clean catalyst treated with oxygen for 15 min at 25°C, the surface oxide made at 300°C is incompletely removed by 5 pulses of hydrogen at 25°C. For the catalyst which has 81% of the Pt atoms exposed, only 1/12 of the surface oxide is removed; for the one having 6.3% exposed, 70% is removed. The effect is thus structure sensitive. The rates of reduction by hydrogen were measured by trapping with hydrogen for various periods. These results correlate with the effect of the pretreatments upon catalytic activity.

In addition, an extensive series of experiments was conducted by Professor Butt's group on the series of Pt/SiO_2 catalysts to determine the effects of pretreatment procedures on activity for methylcyclopropane (MCP) hydrogenation. Each sample of the series was reduced in hydrogen at temperatures ranging from 25 to 450°C and then tested for activity at 0°C and 15/1 hydrogen/hydrocarbon ratio. Hydrogenation activity was enhanced by low temperature reduction for the catalysts of lower dispersion, while high temperature reduction enhanced activity of the high dispersion (63% and 81%) samples. While the activity levels are affected by the pretreatment procedures, preliminary results with 7.1% and 63% dispersion samples indicate that the activation energy for MCP hydrogenation is unaffected.

Efforts continued in Professor Cohen's group to develop the proper additives for Pt-Silica gel, to cancel the small-angle x-ray scattering from the gel, so that the surface area of the Pt alone could be measured (without that of the gel). Two promising organic liquids are being tested, which have the same electron density as the gel and low x-ray absorption. We are trying to see if they enter the gel easily and do not evaporate quickly.

Previously, they had measured the mean square thermal vibrations (u^2) of the Pt atoms in the catalysts by integrating several Pt Bragg peaks at room temperature (I) and determining the slope of ln I vs $(\sin_2 \theta)/\lambda^2$ (where θ is the scattering angle and λ the x-ray wavelength). This slope is 16 π^2 (u^2). The peaks are quite broad for the smaller catalyst sizes. As a result, a decreased (I) may not be due to increased vibrations, but due to our inability to find the tails of a peak. Accordingly, we have examined a 220 peak at both room temperature and 77°K, for the sample with 27% dispersion. The ratio was 1.21 $(I_{77^\circ K}/I_{RT})$ which is in reasonable agreement with the ratio predicted from the other measurements, 1.12. Therefore, our results on the large increase in thermal vibrations with decreasing size are substantiated.

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